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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Organic Metal Compounds and Processes for Making such Compounds

We, IONS EXCHANGE AND CHEMICAL CORP., of 105—107, Chambers Street, New York 7, New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to organic metal compounds and to a process for making such compounds from suitable polymeric starting materials, such as cellulose, thermoplastic resins, and elastomers.

The invention has for its object to provide a process for treating such starting materials for the purpose of improving their physical characteristics (as by increasing their tensile strength) and/or imparting to them desirable chemical properties (such as greater oxidation resistance); it has also been discovered that a process according to the invention may be used for the production of antiseptic agents with high bacteriostatic or germicidal powers.

The invention resides in a process for the production of an organic metal salt, characterised by the treatment of a polymeric starting material, having at least one hydroxyl group, with an aqueous solution of a water-soluble salt of a metal, at a temperature and for a period sufficient to convert said starting material into a solid alcoholate of said metal.

The starting material may be, for example, a gauze or a powder immersed in the aqueous solution, or it may itself be water-soluble and an aqueous solution thereof may be mixed with that of the metal salt.

The invention also resides in an organic metal salt produced by the above process which salt has been found to be an alcoholate of the general form

R—OM

wherein R is a high-polymer radical and M is a monovalent metal or compound of one or more metals.

In certain instances, particularly in the case of nobler metals such as silver, gold, platinum and the like, it is advantageous to start by treating the polymeric starting material with a solution of a relatively base metal and thereafter substituting said base metal with the desired noble metal, by treatment of the pretreated material in a solution of the latter metal. Such substitutions may be undertaken in a single step or in a plurality of stages involving treatment with solutions of progressively more noble metals. Thus the alkali metals, particularly the lighter ones (lithium, sodium and potassium), are well suited to act as preliminary hydrogen substituents preparatorily to substitution by one of the nobler metals, e.g., silver; they need, in fact, not be incorporated into the organic starting material in a separate treatment stage but may be admixed, as catalytic agents, with the aqueous solution of the nobler metal. Suitable aqueous solutions of these alkali metals include solutions of sodium (or potassium), thiosulfate or, preferable, solutions of compounds of these metals with lower hydrocarbons, such as sodium (or potassium) acetate.

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Since the process according to the invention involves the substitution of a relatively easily replaceable hydrogen atom in a hydroxyl group, the resulting product will (at least, in the case of relatively noble metals, standing above hydrogen in the electromotive series) be generally more resistant to chemical attacks than the unmodified starting material; a certain improvement in mechanical strength will also be observed in many instances. At the same time, the overall general appearance of the ultimate compound will differ but little from that of the starting material, except that a change in color will frequently occur.

Furthermore, it appears that the oligodynamic properties of noble metals will be fully present and may even be markedly enhanced in compounds thereof prepared in accordance with this invention, whereby new materials having the physical structure of cellulosic, plastic or elastomeric substances yet endowed with substantial bactericidal and/or fungicidal powers will be obtained. The process of the invention, if applied to high-polymer starting materials in powder form (e.g., alpha-cellulose or comminuted polyvinyl alcohol), also lends itself to the manufacture of filter material for the purification of contaminated water and other liquids, which are purified by being brought into contact with an organic salt of an oligodynamic metal produced according to the invention as well as to the production of new types of pigments or opacifiers for lacquers, varnishes and the like. Sheet material treated in accordance with the invention may also be used advantageously as inter-electrode separators for electric cells, the presence of a compound of a relatively noble metal impeding penetration of the separator by ions of a relatively base metal. Thus, a semi-permeable diaphragm comprising a silver salt of regenerated cellulose (for example, as known under the Registered Trade Mark "Cellophane") according to the invention has been found particularly effective to stop zinc penetration in an alkaline battery or accumulator wherein the diaphragm is inserted between a negative zinc electrode and a positive silver electrode.

In the case of salts of oligodynamic metals (such as silver and gold) used as antiseptic agents, it has been found that improved germicidal properties and enhanced penetrating power can be obtained by modifying the simple alcoholate to reduce its capacity for reacting with substances, such as blood, adapted to exert an inhibiting influence upon the antibacterial activity of the agent. One way to accomplish this result is to react the high-polymer starting material with a solution of a complex, preferably organic metal salt in lieu of the simple inorganic salts otherwise employable. Another method resides in the partial substitution of one oligodynamic metal (e.g., silver) by another (e.g., gold), thereby producing complex high-polymer salts of a combination of noble metals, often, the occurrence of the substitution can be conveniently ascertained by observing a change in the color of the material under treatment. A further refinement involves the formation of complex high-polymer salts incorporating a non-metallic active group in addition to the metal substituent. Such salts may be produced by forming an ester from a high-polymer alcohol radical and a radical of an organic or inorganic acid, preferably one having itself germicidal properties (if the final product is to be used for antiseptic purposes). The last-mentioned process can be used to produce germicidal agents effective against anaerobic as well as other organisms.

The invention is applicable to such metals as antimony, cadmium (e.g., for mildew-proofing), chromium, gold, iron (e.g., for the treatment of anaemic persons), magnesium, manganese, platinum, silver, titanium, zinc, zirconium (e.g., for waterproofing), cerium (e.g., as a hemostatic agent) and other rare-earth metals. Also, it appears that any polymeric material having one or more hydroxyl groups will act as a suitable starting material, yet that cellulose (e.g., in the form of cotton gauze, cellulose sheets or alpha-cellulose powder) represents a preferred starting material by reason of its greater affinity for the metal solutions employed. It is for this reason that cellulosic starting materials have been described in most of the following examples.

Example I.

Cotton gauze is steeped in an aqueous solution of 1% silver nitrate $AgNO_3$ containing 0.7% sodium acetate CH_3COONa. The immersion is continued for thirty minutes at 80° C. whereupon the gauze is washed in water and dried. The resulting product can be used as a self-sterilizing antiseptic bandage.

Example II.

Regenerated cellulose is immersed for an hour in a 1% silver nitrate solution containing 1% potassium acetate CH_3COOK, at a temperature of 70° C., then washed and dried. The resultant

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sheet is adapted to serve as a battery separator.

EXAMPLE III.

Powdered alpha-cellulose is treated for 30 minutes at 100° C. in a solution according to Example II. The resulting powder is washed and dried, then placed in a bag of cotton fibers (treated, if desired, in accordance with Example I) to serve as a purifying agent for liquids; placing this bag in a body of polluted water will serve to decontaminate same in a relatively short period (depending, of course, on the quantity of water, the size of the bag and the amount of agitation present, as well as on the degree of contamination) and will result in a purified liquid which itself, in turn, may be used as a purifying agent for other liquids brought into contact therewith:—

EXAMPLE IV.

Polyvinyl alcohol in powder form is treated in the manner described for alpha-cellulose in Example III, to produce a purifying agent.

EXAMPLE V.

Polyvinyl alcohol is dissolved in water and the resulting solution is mixed with a silver nitrate solution as given in Example I. An antiseptic precipitate results from this treatment.

EXAMPLE VI.

Same as Example V, except that methyl cellulose is used in lieu of polyvinyl alcohol.

EXAMPLE VII.

Cotton gauze as obtained in Example I or a powder as produced in the processes of Example III, IV, V or VI is immersed for twenty seconds in a boiling solution of gold chloride, prepared by dissolving 0.5 grams of gold chloride $AuCl_3.HCl.4H_2O$ in 1 liter of water. After the color of the gauze or powder has changed from brown to violet, the same is removed from the solution and is soaked for several minutes in distilled water, then thoroughly rinsed with tap water and finally allowed to dry. The resulting product has antiseptic and germicidal properties markedly enhanced over those obtainable with the treatment in accordance with the preceding examples.

EXAMPLE VIII.

Alpha-cellulose powder is immersed in a 1% aqueous solution of cadmium sulfate $CdSO_4$, at a temperature of 80° C. and in the presence of sodium thiosulfate $Na_2S_2O_3$ having about the same concentration. The treatment is discontinued after 30 minutes, and the powder thereupon removed from the solution, washed and dried. The result is a powdered compound believed to be a cadmium alcoholate and adapted to be used for mildewproofing.

EXAMPLE IX.

Cotton gauze is immersed in a 1% aqueous solution of magnesium chloride $MgCl_2$, in the presence of sodium acetate CH_3COONa having about the same concentration, at a temperature of 75° C. and for 15 minutes. The gauze is then washed and dried, leaving a white fabric of greater tensile strength than the original gauze. The magnesium alcoholate thus obtained may also be used as an intermediate product in the manufacture of an alcoholate of a noble metal (to be used, for example, as a bacteriostatic or bactericidal agent), such as silver, gold or platinum; thus the magnesium-treated gauze may be further treated in a gold solution according to Example VII.

EXAMPLE X.

Alpha-cellulose powder is immersed in a 1% aqueous solution of manganese chloride $MnCl_2$, in the presence of potassium acetate CH_3COOK and under conditions similar to those set forth in the preceding example. A brownish powder results from this treatment.

EXAMPLE XI.

Regenerated cellulose is steeped in a 1% aqueous solution of titanium sulphate $TiO_2.SO_3$, in the presence of sodium carbonate Na_2CO_3 of similar concentration, for thirty minutes at a temperature of 80° C. A modified cellophane, incorporating what appears to be a titanium alcoholate, is thereby obtained.

EXAMPLE XII.

Regenerated cellulose is immersed in an aqueous titanium chloride solution prepared by dissolving 48 g. of titanium oxide TiO_2 and 26 g. of hydrochloric acid HCl in 1 liter of water; antimony oxide Sb_2O_3 is added in an amount of 100 g. to the above solution, the same being thereupon heated to a temperature of 75° C. The cellulose sheet, having remained for ten minutes in the heated solution, is then washed with a solution of sodium carbonate Na_2CO_3 to neutralize excess acidity, then washed and dried. The resulting sheet material apparently incorporates a titanium-antimony alcoholate with a titanium content of about 8% and a somewhat lesser antimony content, the former being greatly in excess of the titanium content obtainable with the procedure of preceding example.

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EXAMPLE XIII.

Regenerated cellulose is immersed in a 1% aqueous solution of potassium zincate $Zn(OK)_2$ at temperatures of 75° C. and for fifteen minutes, then washed and dried; the result is believed to be a zinc alcoholate.

EXAMPLE XIV.

Polyvinyl alcohol is immersed in a 1% aqueous solution of silver nitrate, in the presence of lithium acetate CH_3COOLi of similar concentration, at 75° C. for thirty minutes. A penetration-resistant separator material is obtained with this treatment.

EXAMPLE XV.

A zinc cellulosate, obtained by the treatment of alpha-cellulose powder with a solution of potassium zincate in the manner described for regenerated cellulose in Example XIII, is steeped in an aqueous solution of a chromium salt, such as a 1% chromium trioxide CrO_3 solution, at 100° C. and for a period of about five minutes. This treatment substantially completely converts the zinc salt into a chromium salt, resulting in a greenish powder.

EXAMPLE XVI.

Alpha-cellulose powder is immersed in a 1% aqueous solution of ferrous chloride $FeCl_2$, at temperatures of 75° C. and for fifteen minutes, then washed and dried. The resultant iron cellulosate powder is believed to be suitable as a carrier for orally administered iron in the treatment of anemia.

EXAMPLE XVII.

An aqueous solution of a rare-earth metal, such as a 2% solution of cerium nitrate $CeNO_3$, is heated to 75° C. and has enough alkali, such as sodium hydroxide NaOH, admixed with it to reduce its p_H to approximately 6.8. Sodium acetate is added in a concentration of approximately 1%. Cotton gauze is steeped in this solution for one hour, then washed and dried. The result is a rare-earth cellulosate.

EXAMPLE XVIII.

A 2% aqueous solution of phosphoric acid H_3PO_4 is heated to the boiling point, whereupon alpha-cellulose powder is immersed therein for twenty minutes. The powder is then washed and dried, until the p_H is neutral, and thereafter treated for thirty minutes in a 1% silver nitrate solution, at 80° C., in the presence of sodium acetate of similar concentration. The final product is strongly germicidal and appears to be particularly effective against anaerobic organisms.

EXAMPLE XIX.

Alpha-cellulose powder is treated in the same manner as in the preceding example, except that a 5% solution of formic acid HCOOH is used instead of the phosphoric acid and the temperature is maintained at 70° C. The powder finally obtained has properties similar to those noted above.

It will be understood that the foregoing examples are representative of processes for the production of a large class of novel, relatively stable compounds obtainable in accordance with this invention by the reaction of cellulose or other alcohols, of polymeric structure, with aqueous solutions of metals not necessarily limited to those specifically enumerated above.

It should be noted that the metal alcoholates produced in accordance with the invention, particularly those of the more noble metals such as silver and gold, are highly inert chemically (except for the property of yielding to substitution by more noble metals as hereinbefore described); thus the antiseptic bandages and other articles herein disclosed will be entirely compatible with known medications, and washing, boiling and similar treatment will not deprive them of their germicidal properties.

Departures from the concentrations, treatment times and temperatures hereinabove set forth are possible; thus, temperatures may range between about 50° and 100° C. and concentrations may vary between fractions of one per cent. and several per cent. by weight (preferably not less than 1/2% and not more than about 2%). A minimum treatment time of 15 to 30 minutes, except with the baser metals or in the case of substitutions, is recommended in most instances, lower temperatures calling, in general, for longer periods.

What we claim is:—

1. A process for producing an organic metal salt, characterised by treating a polymeric starting material, having at least one hydroxyl group, with an aqueous solution of a water-soluble salt of a metal, at a temperature and for a period sufficient to convert the starting material into a solid alcoholate of said metal.

2. A process according to Claim 1, characterised in that the treatment is carried out in the presence of a catalyst.

3. A process according to Claim 2, characterised in that the catalyst is an aqueous solution of a salt of a metal more base than the metal whose organic salt is to be produced.

4. A process according to Claim 3,

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characterised in that the metal of the catalyst is an alkali metal.

5. A process according to Claim 4, characterised in that the alkali metal is one of the elements lithium, sodium and potassium.

6. A process according to Claim 4 or 5, characterised in that the catalyst is a solution of a compound of the alkali metal with a lower hydrocarbon.

7. A process according to Claim 6, characterised in that the catalyst is an acetate of the alkali metal.

8. A process according to Claim 1, characterised by successive treatment of the starting material with solutions of progressively nobler metals.

9. A process according to Claim 1, characterised by a pre-treatment of the starting material with an acid to form an ester.

10. A process according to Claim 9, characterised by pre-treatment with an acid having germicidal properties.

11. A process according to Claim 10, characterised by pre-treatment of the starting material with phosphoric acid, for example, as described in Example XVIII.

12. A process according to Claim 10, characterised by pretreatment of the starting material with formic acid, for example, as described in Example XIX.

13. A process according to any of the preceding claims, characterised in that the treatment is carried out at a temperature ranging between substantially 50 and 100° C.

14. A process according to any of the preceding claims, characterised in that the treatment is continued for a period upwards of substantially five minutes.

15. A process according to any of the preceding claims, characterised in that the starting material is a gauze immersed in the aqueous solution.

16. A process according to any of Claims 1—14, characterised in that the starting material is dissolved in water and mixed with the aqueous solution.

17. A process according to any of Claims 1—14, characterised in that the starting material is a powder immersed in the aqueous solution.

18. An organic metal salt produced by the process according to any of Claims 1—17.

19. An organic metal salt according to Claim 18 in powder form.

20. An organic metal salt according to Claim 18 in gauze form.

21. An organic metal salt according to Claim 18, in the form of a semi-permeable sheet.

22. An organic silver salt according to any of Claims 18—21.

23. A silver cellulosate according to Claim 22.

24. A separator for an electric battery, characterised by comprising a semi-permeable silver cellulosate according to Claims 21 and 23.

25. An organic gold salt according to any of Claims 18—21.

26. An organic rare-earth salt according to any of Claims 18—21.

27. An organic chromium salt according to any of Claims 18—21.

28. An organic titanium salt according to any of Claims 18—21.

29. An organic antimony salt according to any of Claims 18—21.

30. An organic cadmium salt according to any of Claims 18—21.

31. An organic magnesium salt according to any of Claims 18—21.

32. An organic manganese salt according to any of Claims 18—21.

33. An organic platinum salt according to any of Claims 18—21.

34. An organic iron salt according to any of Claims 18—21.

35. An organic zinc salt according to any of Claims 18—21

36. An organic zirconium salt according to any of Claims 18—21.

37. A process for decontaminating polluted liquid, characterised by bringing said liquid into contact with an organic salt of an oligodynamic metal produced by a process according to any of Claims 1—17.

38. A process as set forth in any of the examples.

39. An organic metal salt produced as described in any of the examples.

40. A process substantially as hereinbefore described.

41. An organic metal salt produced substantially as hereinbefore described.

HANS & DANIELSSON,
Chartered Patent Agents,
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